Phoenix Chemistry Classes, Malkapur

UNIT :- IONIC EQUILIBRIA

***Introduction :**An equilibrium between ions and unionized molecules in solution is called ionic equilibrium.

***Electrolyte :** The substances which ionizes & give ions when dissolved in water are called electrolytes. The substances which do not ionize and exist as molecules in aqueous solutions are called as non electrolytes.

*** Strong electrolyte :** The electrolytes which ionizes completely or almost completely are called strong electrolytes. For example: strong acids, strong bases and salts.

E,g, HCl, H_2SO_4, NaOH, KOH, NaCl, KCl.

***Weak electrolyte :** The electrolytes which dissociate to a smaller extent in aqueous solution are called weak electrolytes.

For example: Weak acids and weak bases NH_4OH(ammonium hydroxide), CH_3-COOH

The weak electrolytes dissociate only partially in dilute aqueous solutions. Thus an equilibrium can be established between the ions and non ionized molecules. The ionization reacn is represented as double arrow (⇌)between the ions & non ionized molecule.

*** Degree of dissociation ( ) :** A fraction of total number of moles of an electrolyte that dissociates into its ions in aq. solution at equilibrium is called degree of dissociation.

$$\propto = \frac{\text{number of moles dissociated}}{\text{total number of moles}}$$

Percent dissociation = $\propto$ x 100

If 'c' is the molar concentration of an electrolyte, then equilibrium concentration of cation or anion is ($\propto$ x c) mol dm^{-3}

*** Acids and Bases :-** Acids and bases are familiar chemical compounds. Acetic acid is found in vinegar, citric acid in lemons, magnesium hydroxide in antacids, ammonia in household cleaning products. The tartaric acid is present in tamarind . These are some acids and bases we come across in everyday life.

*** Arrhenius theory of acids and bases:-**

Acid : Acid is a substance which contains hydrogen and gives $H^{\oplus}$ ions in aq. solution

$$HCl_{(aq)} \xrightarrow{water} H^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

$$CH_3COOH_{(aq)} \overset{water}{\rightleftharpoons} CH_3COO^{\ominus}_{(aq)} + H^{\oplus}_{(aq)}$$

Base: Base is a substance that contain OH group and gives hydroxide ions ($OH^{\ominus}$) ions in aqueous solution.

$$NaOH_{(aq)} \rightarrow Na^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$$

$$NH_4OH_{(aq)}) \rightleftharpoons NH_4^{\oplus}((aq) + OH^{\ominus}_{(aq)}$$

Arrhenius theory is applicable only to aqueous solutions. It does not account for the basicity of NH_3 and Na_2CO_3 which do not have OH group.

***Bronsted – Lowry theory :-**

Acid : Acid is a substance that donates a proton ($H^{\oplus}$) to another substance.

Base : base is a substance that accepts a proton ($H^{\oplus}$) from another substance.

For example:

$$HCl + NH_3 \rightleftharpoons NH_4^{\oplus} + Cl^{\ominus}$$

$$Acid_1 \quad Base_2 \quad Acid_2 \quad Base_1$$

In the above reaction HCl and $NH_4^{\oplus}$are proton donors and act as acids. The NH_3 and $Cl^{\ominus}$are proton acceptors and act as bases.

A pair of an acid and a base differing by a proton is said to be a **conjugate acid-base pair.**

$$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

$Acid_1$ $Base_2$ $Acid_2$ $Base_1$

Conjugate acid-base $pair_2$

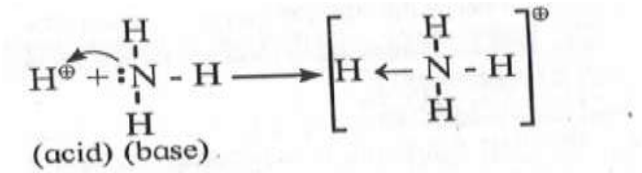
Conjugate acid-base $pair_1$

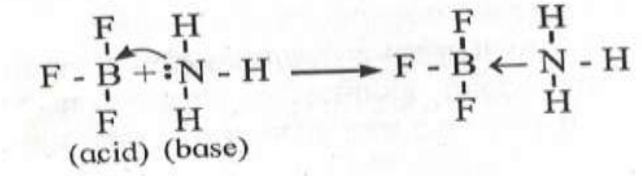
*** Lewis theory :**According to this theory acids and bases are defined as follows.

Acid : Any species that accepts a share in an electron pair is called Lewis acid.

Base : Any species that donates a share in an electron pair is called Lewis base. In short Lewis acids are electron pair acceptors& Lewis bases are electron pair donors.

For example:





All Bronsted bases are also Lewis bases, but all Bronsted acids are not Lewis acids.

Amphoteric nature of water : Water has the ability to act as an acid as well as a base. Such behaviour is known as amphoteric nature of water. For example:

$H_2O_{(l)} + NH_{3\,(aq)} \rightleftharpoons OH^{\ominus}_{(aq)} + NH_4^{\oplus}(aq)$

Acid

$H_2O_{(l)} + HCl_{(aq)} \rightleftharpoons H_3O^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$

Base

H_2O acts as an acid towards NH_3 and as a base towards HCl. Therefore H_2O is amphoteric.

***Ionisation of acids and bases :-**

Acids and bases are classified as strong acid and strong bases, weak acids and weak bases on the basis of their **extent of dissociation**. Strong acids and bases are almost completely dissociated in water. For example:

$HCl_{(aq)} \rightarrow H^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$

$NaOH_{(aq)} \rightarrow Na^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$

Typical strong acids are HCl, HNO_3, H_2SO_4, HBr and HI while typical strong bases are NaOH and KOH.

Weak acids and weak bases are partially dissociated in water. The solution of a weak acid or a weak base contains undissociated molecules along with a small number of ions at equilibrium. For example:

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^{\ominus}_{(aq)} + H^{\oplus}_{(aq)}$

$NH_4OH_{(aq)} \rightleftharpoons NH_4^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$

Note that HCOOH(formic acid), HF, H_2S are examples of weak acids while $Fe(OH)_3$, $Cu(OH)_2$ are examples of weak bases.

*** Dissociation constant of weak acids and weak bases :-** The dissociation of a weak acid HA in water is expressed as

$HA_{(aq)} \rightleftharpoons H^{\oplus}_{(aq)} + A^{\ominus}_{(aq)}$

The equilibrium constant called dissociation constant of acid for this equilibrium is :

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

Similiarly the dissociation of weak base BOH in water is represented as :

$BOH_{(aq)} \rightleftharpoons B^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$

The equilibrium constant called dissociation constant of base for this equilibrium is ,

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}$$

Thus, the dissociation constant of a weak acid or weak base is defined as the equilibrium constant for dissociation equilibrium of weak acid or weak base, respectively.

*** Ostwald's dilution law :** Arrhenius concept of acids and bases was expressed quantitatively by F,W, Ostwald in the form of the dilution law in 1888.

a) Weak acids : Consider an equilibrium of weak acid HA that exists in solution partly as the undissociated species HA and partly $H^{\oplus}$ and $A^{\ominus}$ ions. Then

$HA_{(aq)} \rightleftharpoons H^{\oplus}_{(aq)} + A^{\ominus}_{(aq)}$

The acid dissociation constant is given by

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} \text{----(I)}$$

Suppose 1 mol of acid HA is initially present in volume V dm^3 of the solution. At equilibrium the fraction dissociated would be $\propto$, where $\propto$ is degree of dissociation of the acid.

The fraction of an acid that remains undissociated would be (1 - $\propto$).

	$HA_{(aq)} \rightleftharpoons$	$H^{\oplus}_{(aq)} +$	$A^{\ominus}_{(aq)}$
Amount present at equilibrium /mol	(1-$\propto$)	$\propto$	$\propto$
Concentration at equilibrium /mol dm^{-3}	$\frac{1-\propto}{V}$	$\frac{\propto}{V}$	$\frac{\propto}{V}$

Thus, at equilibrium $[HA] = \frac{1-\propto}{V}$, mol dm^{-3},

$[H^{\oplus}] = [A^{\ominus}] = \frac{\propto}{V}$ mol dm^{-3}.

Substituting these in -----(I)

$$K_a = \frac{(\propto/v)(\propto/v)}{(1-\propto)/V} = \frac{\propto^2}{(1-\propto)V} \quad \text{.....(II)}$$

If c is the initial concentration of an acid in mol dm^{-3} then c = 1/V.

Replacing 1/V in Eq. (II) by c we get

$K_a = \frac{\alpha^2 c}{1-\alpha}$ .....(III)

For the weak acid HA, α is very small, or $(1 - \alpha) \cong 1$. With this Eq. (II) and (III) reduce.

$K_a = \alpha^2/V$ and $K_a = \alpha^2 c$

$\alpha = \sqrt{\frac{Ka}{c}}$ or $\alpha = \sqrt{K_a V}$ OR $\alpha \alpha \sqrt{\frac{1}{c}}$ **or** $\alpha \alpha \sqrt{V}$

Thus degree of dissociation of a weak acid is inversely prop. to the square root of its conc^n or directly prop. to the square root of volume of the solution containing 1 mol of the weak acid.

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b) Weak base : Consider 1 mol of weak base BOH dissolved in V dm^3 of solution. The base dissociates partially as

$BOH_{(aq)} \rightleftharpoons B^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$

The base dissociation constant is

$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}$ ----- I

Let the fraction dissociated at equilibrium is α and that remains undissociated is $(1 - \alpha)$.

$BOH_{(aq)} \rightleftharpoons B^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$			
Amount present at equilibrium	$(1-\alpha)$	α	α
Concentration at equilibrium	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

A equilibrium,

$[BOH] = \frac{1-\alpha}{V}$ moldm^{-3}, $[B^{\oplus}] = [OH^{\ominus}] = \frac{\alpha}{V}$ moldm^{-3}

Substitution of these concentrations in Eq. (I), gives

$K_b = \frac{(\alpha/v)(\alpha/v)}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V}$ .....(II)

If c is the initial conc. of a base in mol dm^{-3} then $c = 1/V$. Replacing 1/V in Eq. (II) by c, we get

$K_b = \frac{\alpha^2 c}{(1-\alpha)}$ ..... (III) For the weak base BOH, α is very small, or $(1 - \alpha) \cong 1$. With this Eq. (II) and (III) reduce.

$K_b = \alpha^2/V$ and $K_b = \alpha^2 c$

$\alpha = \sqrt{K_b V}$, $\alpha = \sqrt{\frac{K_b}{c}}$ OR $\alpha \alpha \sqrt{\frac{1}{c}}$ **or** $\alpha \alpha \sqrt{V}$

The degree of dissociation of a weak base is inversely prop. to square root of its conc^n & is directly prop. to square root of volume of the solution containing 1 mol of weak base.

***Autoionization of water :-** Pure water ionizes to a very small extent. The ionization equilibrium of water is represented as,

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$

The equilibrium constant (K) for the ionization of water is given by

$K = \frac{[H_3O^{\oplus}][OH^{\ominus}]}{[H_2O(l)]^2}$ .....(I)

Or $K[H_2O]^2 = [H_3O^{\oplus}][OH^{\ominus}]$ .....(II)

A majority of H_2O molecules are undissociated, consequently concentration of water $[H_2O]$ can be treated as constant. Then

$[H_2O]^2 = K'$. Substituting this in Eq. (II) we get,

$K \times K' = [H_3O^{\oplus}][OH^{\ominus}]$ .....

$K_w = [H_3O^{\oplus}][OH^{\ominus}]$

Where $K_w = KK'$ is called ionic product of water.

The product of molar concentration of hydronium (or hydrogen ions) and hydroxyl ions at equilibrium in pure water at the given temperature is called ionic product of water.

In pure water $H_3O^{\oplus}$ ion concentration always equals the concentration of $OH^{\ominus}$ ion. Thus at 298 K this concentration is found to be 1.0×10^{-7}mol/L.

$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7})$

$K_w = 1.0 \times 10^{-14}$

***pH scale :-**Sorensen in 1909 defined the pH of a solution as the negative logarithm to the base 10, of the concentration of $H^{\oplus}$ ions in solution in mol dm^{-3}. It is mathematically expressed as

$pH = -\log_{10}[H^{\oplus}]$ ------(I)

Similarly pOH of a solution can be defined as the negative logaritham to the base 10, of the molar concentration of $OH^{\ominus}$ ions in solution.

Thus, $pOH = -\log_{10}[OH^{\ominus}]$ .....(II)

Relationship between pH and pOH:-

The ionic product of water is

$K_w = [H_3O^{\oplus}][OH^{\ominus}]$

Now, $K_w = 1.0 \times 10^{-14}$ at 298 K and thus

$[H_3O^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14}$

Taking logarithm of both the sides, we write

$\log_{10}[H_3O^{\oplus}] + \log_{10}[OH^{\ominus}] = -14$

$-\log_{10}[H_3O^{\oplus}] + \{-\log_{10}[OH^{\ominus}]\} = 14$ ..... Since

$pH = -\log_{10}[H_3O^{\oplus}]$ & $pOH = -\log_{10}[OH^{\ominus}]$

$pH + pOH = 14$

***Acidity ,basicity & neutrality of aq.sol^n:-**

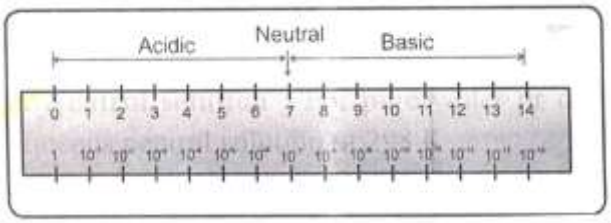
1) Neutral solution : For pure water or any aqueous neutral solution at 298 K

$[H_3O^{\oplus}]=[OH^{\ominus}] = 1.0 \times 10^{-7}$ M

Hence, pH = $-\log_{10}[H^{\oplus}] = -\log_{10}[1 \times 10^{-7}] = 7$

2) Acidic solution : In acidic solution, there is excess of $H_3O^{\oplus}$ ions, or $[H_3O^{\oplus}] > [OH^{\ominus}]$ Hence, $[H_3O^{\oplus}] > 1.0 \times 10^{-7}$with pH < 7.

3) Basic solution : In basic solution, the excess of $OH^{\ominus}$ ions are present i.e. $[H_3O^{\oplus}]<[OH^{\ominus}]$ or $[H_3O^{\oplus}] < 1.0 \times 10^{-7}$ with pH > 7.



*** Hydrolysis of salts :- * Types of salts**

These are of four types

1) Salts derived from **strong acid and strong base.** E,g, :NaCl, Na_2SO_4, $NaNO_3$, KCl, KNO_3.

2) Salts derived from **strong acids and weak bases**. . E,g: NH_4Cl, $CuSO_4$, NH_4NO_3, $CuCl_2$.

3) Salts derived from **weak acids and strong bases**. . E,g: CH_3COONa, KCN, Na_2CO_3.

4) Salts derived from **weak acids and weak bases**.. E,g: CH_3COONH_4 , NH_4CN., NH_4F

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* **Concept of Hydrolysis :-** Hydrolysis of salt is defined as the reaction in which cations or anions or both ions of a salt react with ions of water to produce acidity or alkalinity (or sometimes even neutrality).

*** Salts of strong acid and strong bases :-**

NaCl is a salt of strong acid HCl and a strong base NaOH. When it is dissolved in water, it dissociates completely into its ions.

$NaCl\ (aq) \rightarrow Na^{\oplus}(aq) + Cl^{\ominus}(aq)$

The ions $Na^{\oplus}$ and $Cl^{\ominus}$ have no tendency to react with water. This is because the possible products NaOH and HCl of such reactions are strong electrolytes and dissociate completely in aqueous solutions.

In other words,

$Na^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)} + H_2O \rightarrow \underset{\text{(Strong acid)}}{HCl_{(aq)}} + \underset{\text{(Strong base)}}{NaOH_{(aq)}}$

[possible products]

$HCl_{(aq)} + NaOH_{(aq)} + H_2O \rightarrow H_3O^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)} + Na^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$

Thus the reactants and the products are the same. This implies that neither the cation nor anion of the salt reacts with water or there is no hydrolysis. Equality of $H_3O^{\oplus} = OH^{\ominus}$ produced by ionization of water is not disturbed and solution is neutral. It may be concluded that salt of strong acid and strong base does not undergo hydrolysis.

*** Salts of strong acids and weak bases :-**

$CuSO_4$ is salt of strong acid H_2SO_4 and weak base $Cu(OH)_2$. When $CuSO_4$ is dissolved in water, it dissociates completely as,

$CuSO_{4\ (aq)} \rightarrow Cu^{2\oplus}_{(aq)} + SO_4^{2\ominus}{}_{(aq)}$

$SO_4^{2\ominus}{}_{(aq)}$ ions of salt have no tendency to react with water because the possible product H_2SO_4 is strong electrolyte. The reaction of $Cu^{2\oplus}$ ions with $OH^{\ominus}$ ions form unionized $Cu(OH)_2$. The hydrolytic equilibrium for $CuSO_4$ is then written as,

$Cu^{2\oplus}_{(aq)} + 4H_2O_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2H_3O^{\oplus}_{(aq)}$

Due to the presence of excess of $H_3O^{\oplus}$ ions, the resulting solution of $CuSO_4$ becomes acidic and turns blue litmus red.

Formation of sparingly soluble $Cu(OH)_2$ by hydrolysis makes the aqueous solution of $CuSO_4$ turbid. If H_2SO_4, that is $H_3O^{\oplus}$ ions are added, hydrolytic equilibrium shifts to the left. A turbidity of $Cu(OH)_2$ dissolves to give a clear solution. To get clear solution of $CuSO_4$, the addition of H_2SO_4 would be required.

*** Salts of weak acids and strong bases:-**

CH_3COONa is a salt of weak acid CH_3COOH and strong base NaOH, when dissolved in water, it dissociates completely.

$CH_3COONa_{(aq)} \rightarrow CH_3COO^{\ominus}_{(aq)} + Na^{\oplus}_{(aq)}$

Water dissociates slightly as,

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$

Solution of CH_3COONa contains $Na^{\oplus}$, $H_3O^{\oplus}$,$CH_3COO^{\ominus}$,$OH^{\ominus}$. The $Na^{\oplus}$ ions of salt have no tendency to react with $OH^{\ominus}$ ions of water since the possible product of the reaction is NaOH, a strong electrolyte. On the other hand the reaction of $CH_3COO^{\ominus}$ ions of salt with

the $H_3O^{\oplus}$ ions from water produces unionized CH_3COOH.

$CH_3COO^{\ominus}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^{\ominus}$

Thus, hydrolytic equilibrium for CH_3COONa is,

$CH_3COONa_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + Na^{\oplus}_{(aq)} + OH^{\ominus}_{(aq)}$

As a result of excess $OH^{\ominus}$ ions produced the solution becomes basic. The solution of CH_3COONa is therefore basic.

Remember :-As a general rule, the solutions of salts of strong acids and strong bases are neutral, the solutions of salts of strong acid and weak bases are acidic and the solutions of salts of strong bases and weak acids are basic.

*** Salts of weak acids and weak bases :-**

When salt BA of weak acid HA and weak base BOH is dissolved in water, it dissociates completely as

$BA_{(aq)} \rightarrow B^{\oplus}_{(aq)} + A^{\ominus}_{(aq)}$

The Hydrolysis reaction involves the interaction of both the ions of the salt with water,

$B^{\oplus}_{(aq)} + A^{\ominus}_{(aq)} + H_2O \rightleftharpoons \underset{\text{(weak base)}}{BOH} + \underset{\text{(weak acid)}}{HA}$

The solution may turn out acidic, basic or neutral depending on the relative strength of weak base and weak acid formed in the hydrolysis.

i) if, $K_a > K_b$, the solution will be slightly acidic.

ii) If, $K_a < K_b$, the solution will be slightly basic.

iii) If ,$K_a = K_b$,the solution will be neutral.

I) Salt of weak acid & weak base for which $K_a > K_b$:-

NH_4F is a salt of weak acid HF (K_a=7.2x10^{-4}) and weak base NH_4OH (K_b = 1.8 x 10^{-5}). Here, K_a is greater than K_b. The salt hydrolyses as

$NH_4^{\oplus}{}_{(aq)} + F^{\ominus}_{(aq)} + H_2O \rightleftharpoons \underset{\text{(weak base)}}{NH_4OH_{(aq)}} + \underset{\text{(weak acid)}}{HF_{(aq)}}$

The acid HF is slightly stronger than base NH_4OH. The two ions react with water as

$NH_4^{\oplus}{}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_3O^{\oplus}_{(aq)}$

$F^{\ominus}_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^{\ominus}_{(aq)}$

The $NH_4^{\oplus}$ ions hydrolyse to a slightly greater extent than the $F^{\ominus}$ ions. That means the reaction produces more $H_3O^{\oplus}$ ions than the $OH^{\ominus}$ ions produced in above reaction

The solution of NH_4F is thus only slightly acidic and turns blue litmus red.

II) Salt of weak acid and weak base for which $K_a < K_b$:-

NH_4CN is the salt of weak acid HCN (K_a = 4.0 x 10^{-10}) and weak base NH_4OH (K_b = 1.8 x 10^{-5}) showing that $K_a < K_b$. When NH_4CN is dissolved in water, it hydrolyses as

$NH_4^{\oplus}{}_{(aq)} + CN^{\ominus}_{(aq)} + H_2O_{(l)} \rightleftharpoons \underset{\text{(weak base)}}{NH_4OH_{(aq)}} + \underset{\text{(weak acid)}}{HCN_{(aq)}}$

The base NH_4OH is stronger than the acid HCN. The ions of the salt react with water as,

$NH_4^{\oplus}{}_{(aq)} + 2\,H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_3O^{\oplus}_{(aq)}$

$CN^{\ominus}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^{\ominus}_{(aq)}$

The $CN^{\ominus}$ ions hydrolyse to a greater extent than $NH_4^{\oplus}$ions, that means the reaction produces more $OH^{\ominus}$ ions than the $H_3O^{\oplus}$ ions produced in above reaction . The solution of NH_4CN is basic and turns red litmus blue.

III) Salt of weak acid and weak base for which $K_a = K_b$.

:- CH_3COONH_4 is a salt of weak acid, CH_3COOH (K_a =1.8 x 10^{-5}) and weak base, NH_4OH (K_b = 1.8 x 10^{-5}). When the salt CH_3COONH_4 is dissolved in water, it undergoes hydrolysis as…

$CH_3COO^{\ominus}_{(aq)} + NH_4^{\oplus}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons \underset{\text{(weak acid)}}{CH_3COOH_{(aq)}} + \underset{\text{(weak base)}}{NH_4OH_{(aq)}}$

The ions of the salt react with water as

i) $CH_3COO^{\ominus}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^{\ominus}_{(aq)}$

ii) $NH_4^{\oplus}{}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_3O^{\oplus}_{(aq)}$

As $K_a = K_b$, the relative strength of acid and base produced in hydrolysis is the same. Therefore, the solution is neutral. Hydrolysis of $NH_4^{\oplus}$ produces as many $H_3O^{\oplus}$ ions as that of $CH_3COO^{\ominus}$produces $OH^{\ominus}$ ions.

Buffer solutions :- Buffer solution is defined as a solution which resists drastic changes in pH value when a small amount of strong acid or strong base or water is added to it.

*** Types of buffer solutions :-**

There are two types of buffer solutions. Acidic buffer used to maintain an acidic pH, while basic buffer maintains alkaline pH.

a) Acidic buffer solution : A solution containing a weak acid & its salts with strong base is called acidic buffer solution.

For example: A solution containing weak acid such as CH_3COOH and its salt such as CH_3COONa is an acidic buffer solution.

pH of acidic buffer is given by the equation

$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$ .....

where $pK_a = - \log_{10} K_a$ .....

and K_a is the dissociation constant of the acid.

b) Basic buffer solution :- A solution containing a weak base and its salt with strong acid is the basic buffer solution.

For example : a solution containing a weak base such as NH_4OH and its salt such as NH_4Cl is a basic buffer solution.

The pOH of basic buffer is given by,

$pOH = pK_b + \log_{10} \frac{[salt]}{[base]}$ .....

Where $pK_b = - \log_{10} K_b$ .....

and K_b is the dissociation constant for the base.

The above equation used to determine pH & pOH of buffer solution is called **Henderson Hasselbalch equation.**

*** Buffer action :** Let us consider sodium acetate -acetic acid buffer. Here sodium acetate is a strong electrolyte which dissociates completely in water producing large concentration of $CH_3COO^{\ominus}$ as follows:

$CH_3COONa(aq) \rightarrow CH_3COO^{\ominus}(aq) + Na^{\oplus}(aq)$

On the other hand since the acetic acid is a weak acid, the concentration of undissociated CH_3COOH molecules is usually high. If a strong acid is added to this solution the added $H^{\oplus}$ ions will be consumed by the conjugate base $CH_3COO^{\ominus}$ present in large concentration.

$CH_3COO^{\ominus}{}_{(aq)} + H^{\oplus}{}_{(aq)} \rightarrow CH_3COOH_{(aq)}$

(large concentration) (added acid)

Similarly, if small amount of base is added, the added $OH^{\ominus}$ ions will be neutralized by the large concentration of acetic acid as shown in the following reactions...

$CH_3COOH_{(aq)} + OH^{\ominus}{}_{(aq)} \rightarrow CH_3COO^{\ominus}{}_{(aq)} + H_2O$

(large concentration) (added base)

The acid or base added thus cannot change the $[H^{\oplus}]$ or $[OH^{\ominus}]$ concentrations and, pH of the buffer remains unchanged. Dilution does not have any effect on pH of buffer.

*** Properties of buffer solution**

The pH of a buffer solution does not change appereciably

i) by addition of small amount of either strong acid or strong base, ii) On dilution or iii) when it is kept for long time.

Applications of buffer solution

i) In biochemical system :- pH of blood in our body is maintained at 7.36 – 7.42 due to ($HCO_3^{\ominus} + H_2CO_3$) buffer. A small change of 0.2 pH units can cause death. The saline solution used for intravenous injection must contain buffer system to maintain the proper pH of the blood.

ii) Agriculture:- The soils get buffered due to presence of salts such as carbonate, bicarbonate, phosphates and organic acids. The choice of fertilizers depends upon pH of soil.

iii) Industry :- Buffers play an important role in paper, dye, ink, paint and drug industries.

iv) Medicine:- Penicillin preparations are stabilized by addition of sodium citrate as buffer. When citric acid is added to milk of magnesia ($Mg(OH)_2$), magnesium citrate is formed, which is a buffer.

v) Analytical chemistry :- In qualitative analysis, a pH of 8 to 10 is required for precipitation of cations IIIA group. It is maintained with the use of ($NH_4OH + NH_4Cl$) buffer.

*** Solubility product:-**

Suppose some powdered sparingly soluble salt such as AgCl is put into water and stirred vigorously. A very small amount of AgCl dissolves in water to form its saturated solution. Most of the salt remains undissolved.

A dynamic equilibrium exists between undissolved (solid) AgCl and the dissolved ions, $Ag^{\oplus}$ and $Cl^{\ominus}$, in the saturated solution

This equilibrium, called solubility equilibrium, is represented as :

$AgCl_{(s)} \rightleftharpoons Ag^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$

The expression for its equilibrium constant is :

$$K = \frac{[Ag^{\oplus}][Cl^{\ominus}]}{[AgCl]} \quad \ldots\ldots\ldots\ldots (I)$$

The concentration of undissolved solid AgCl is constant … we may write

$[AgCl]$ = constant = K'

Substituting in Eq. (I) we write

$$K = \frac{[Ag^{\oplus}][Cl^{\ominus}]}{K'}$$

$$K \times K' = [Ag^{\oplus}][Cl^{\ominus}]$$

The product of K x K' is another constant and is called solubility product. It is denoted by K_{sp}.

$$K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$$

For the general salt solubility equilibrium

$B_xA_y(s) \rightleftharpoons xB^{y\oplus}_{(aq)} + yA^{x\ominus}_{(aq)}$

The solubility product is

$$K_{sp} = \left[B^{y\oplus}\right]^x \left[A^{x\ominus}\right]^y$$

The product of equilibrium concentrations of the constituent ions raised to the power equal to their respective coefficients in the balanced equilibrium expression at a given temperature is called solubility product.

Consider following examples.

i) $BaSO_{4(s)} \rightleftharpoons Ba^{2\oplus}_{(aq)} + SO_4^{2\ominus}{}_{(aq)}$

$$K_{sp} = [Ba^{2\oplus}][SO_4^{2\ominus}]$$

ii) $CaF_{2(s)} \rightleftharpoons Ca^{2\oplus}(aq) + 2F^{\ominus}(aq)$

$$K_{sp} = [Ca^{2\oplus}][F^{\ominus}]^2$$

iii) $Bi_2S_{3\,(s)} \rightleftharpoons 2Bi^{3\oplus}{}_{(aq)} + 3S^{2\ominus}{}_{(aq)}$

$$K_{sp} = [Bi^{3\oplus}]^2[S^{2\ominus}]^3$$

iv) $Ca_3(PO_4)_{2\ (s)} \rightleftharpoons 3Ca^{2\oplus}_{(aq)} + 2PO_4^{3\ominus}{}_{(aq)}$

$$K_{sp} = [Ca^{2\oplus}]^3[PO_4^{3\ominus}]^2$$

Molar solubility :- The number of moles of a compound that dissolve to give one litre of saturated solution is called its molar solubility.

$$\text{Molar solubility (mol/L)} = \frac{\text{solubility in g/L}}{\text{molar mass in g/mol}}$$

Consider once again the solubility equilibrium for B_xA_y,

$B_xA_y(s) \rightleftharpoons xB^{y\oplus}_{(aq)} + yA^{x\ominus}_{(aq)}$

The solubility product is given by:

$$K_{sp} = \left[B^{y\oplus}\right]^x \left[A^{x\ominus}\right]^y \text{-------(I)}$$

If S is the molar solubility of the compound, the equilibrium concentrations of the ions in the saturated solution will be

$\left[B^{y\oplus}\right]$ = xS mol/L & $\left[A^{x\ominus}\right]$ = yS mol/L

From Eq.(I) $K_{sp} = [xS]^x[yS]^y = x^xy^yS^{x+y}$ **Ex.**

i) For AgBr $AgBr_{(s)} \rightleftharpoons Ag^{\oplus}_{(aq)} + Br^{\ominus}_{(aq)}$

Here, x = 1, y = 1 $\therefore K_{sp} = S \times S = S^2$

ii) For PbI_2 , $PbI_{2(s)} \rightleftharpoons Pb^{2\oplus}_{(aq)} + 2I^{\ominus}_{(aq)}$

X = 1, y = 2, $\therefore K_{sp} = (1)^1(2)^2S^{1+2} = 4S^3$

iii) $Al(OH)_3$ $Al(OH)_{3(s)} \rightleftharpoons Al^{3\oplus}_{(aq)} + 3OH^{\ominus}_{(aq)}$

X = 1, y = 3 $\therefore K_{sp} = (1)^1(3)^3S^{1+3} = 27S^4$

Condition of precipitation :- Ionic product (IP) of an electrolyte is defined in the same way as solubility product (K_{sp}). The only difference is that the ionic product expression contains concentration of ions under any condition whereas expression of K_{sp} contains only equilibrium concentrations. If,

a. I P = K_{sp}; the solution is saturated and solubility equilibrium exists.

b. I P > K_{sp}; the sol^n is supersaturated & hence precipitation of the compound will occur.

c. If I P < K_{sp}, the solution is unsaturated and precipitation will not occur.----------

Common ion effect :-Consider a sol^n of weak acid CH_3COOH & its soluble salt CH_3COONa.

CH_3COOH is weak acid, dissociates only slightly in sol^n $CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}_{(aq)}$

CH_3COONa being a strong electrolyte dissociates almost completely in solution.

$CH_3COONa_{(aq)} \rightarrow CH_3COO^{\ominus}{}_{(aq)} + Na^{\oplus}{}_{(aq)}$

Both the acid and the salt produce $CH_3COO^{\ominus}$ ions in solution. Therefore it provides high concentration of $CH_3COO^{\ominus}$ions.

According to Le-Chatelier principle, the addition of $CH_3COO^{\ominus}$ from CH_3COONa to the solution of CH_3COOH, shifts equilibrium of dissociation of CH_3COOH to left. Thus reverse reaction is favoured in which $CH_3COO^{\ominus}$ combines with $H^{\oplus}$ to form unionized CH_3COOH. Hence dissociation of CH_3COOH is suppressed due to presence of CH_3COONa containing a common $CH_3COO^{\ominus}$ ion.

The common ion effect is defined as the ionization of a weak electrolyte is suppressed in presence of a strong electrolyte containing an ion common to the weak electrolyte.

*** Common ion effect & solubility :-**

The presence of a common ion also affects the solubility of a sparingly soluble salt. Consider, the solubility equilibrium of AgCl,

$AgCl_{(s)} \rightleftharpoons Ag^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$

The solubility product of AgCl is

$$K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$$

Suppose $AgNO_3$ is added to the saturated solution of AgCl. The salt $AgNO_3$ being a strong electrolyte dissociates completely in the solution. $AgNO_{3(aq)} \rightarrow Ag^{\oplus}_{(aq)} + NO_3^{\ominus}{}_{(aq)}$

The dissociation of AgCl and $AgNO_3$ produce a common $Ag^{\oplus}$ ion. The concentration of $Ag^{\oplus}$ ion in the solution increases owing to complete dissociation of $AgNO_3$. According to Le-chatelier's principle the addition of $Ag^{\oplus}$ ions from $AgNO_3$ to the solution of AgCl shifts the solubility equilibrium of AgCl from right to left. The reverse reaction in which AgCl precipitates, is favoured until solubility equilibrium is re-established. The value of K_{sp} however, remains the same since it is an equilibrium constant. The solubility of a sparingly soluble compound, thus decreases with the presence of a common ion in solution.

Problems: - 1) A weak monobasic acid is 0.05 % dissociated in 0.02 M solution. Calculate dissociation const. of acid.

2)Dissociation const. of NH_4OH is 1.8×10^{-5}. Calculate its degree of dissociation in 0.01 M. sol^n.

3) A weak monobasic acid is 12% dissociated in 0.05 M sol^n. What is % dissociation in 0.15 M sol^n.

4) Calculate $[H_3O^{\oplus}]$ in 0.1 mol.dm^{-3} solution of acetic acid if dissociation constant is 1.8×10^{-5}.

5) An acid is 5% ionized in its decimolar solution. Calculate dissociation constant of acid.

6) Dissociation const. of acetic acid is 1.8×10^{-5}. Calculate % dissoci^n of acetic acid in 0.01 M sol^n.

pH & pOH:- 1) Calculate pH & POH of 0.01 M HCl.

2) Calculate pH & POH of 0.01 M H_2SO_4 solution.

3) pH of a solution is 4.12 Calculate the $[H_3O^{\oplus}]$ ion.

4) A weak monobasic acid is 0.04 % dissociated in 0.025 M solution. Find pH of the sol^n.

5) pH of a sol^n is 6.06 calculate its $[H_3O^{\oplus}]$ ion .

6) The pH of a weak monobasic acid is 3.2 in its 0.02 M sol^n. Calculate its dissociation constant.

7) In NaOH solution, $[OH^{\ominus}]$ is 2.87×10^{-4}. find pH .

8) The pH of rain water collected in certain region of Maharashtra on particular day was 5.1 Calculate the $[H^{\oplus}]$ of the rain water & its percent dissociati^n.

9) The pH of monoacidic base is 11.2 calculate its percent dissociation in 0.02 M solution.

10) The pH of a monobasic acid is 4.7. Calculate dissociation constant in 0.015 M sol^n.

11) The solubility product of AgBr is 5.2×10^{-13}. Calculate its solubility in mol.dm^{-3} & in g.dm^{-3} [Molar mass of AgBr = 187.8 g/mol]

12) If 20.0 cm^3 of 0.050 M $Ba(NO_3)_2$ are mixed with 20.0 cm^3 of 0.020 M NaF, will BaF_2 precipitate? [K_{sp} of BaF_2 is 1.7×10^{-6} at 298 K.]

13) A solution is prepared by mixing equal volume of 0.1 M $MgCl_2$. & 0.3 M $Na_2C_2O_4$ at 293 K. Would MgC_2O_4 precipitate out ?
[K_{sp} of MgC_2O_4 at 293 k is 8.56×10^{-5} .]

Board questions:-

Feb. 2025 :- 1)Define conjugate acid- base pair. The hydroxyl ion conc. in aq. sol^n of NaOH is 2×10^{-4} mol/dm^3. Calculate pH of sol^n

2)Which formula correlates degree of dissociation & conc^n of electrolyte

a) $c = \sqrt{\frac{K_a}{\propto}}$ b) $\propto = \sqrt{\frac{K_a}{c}}$ c) $c = \sqrt{Ka. \propto}$ d) $c = \sqrt{\frac{\propto}{Ka}}$

3)Explain common ion effect.

July-24 :- 1)Obtain the relation between solubility product & its solubility for $Al(OH)_3$

2) PH of 0.001 M HCl sol^n is …a) 4 b)3 c) 2 d)1

3) Define Buffer soln **,**write HendrsonHasselbalch equation for acidic buffer . 4) Derive Ostwalds dilution law for weak acid **(j- 22,23,24)**

Feb 2024 :-1)Define acids &bases according to Bronsted- Lowry Theory**.**

2) Derive the relationship bet^n pH & pOH**. (feb-22)**

3) Explain buffer action of sodium acetate-acetic acid buffer. **4)** The PH of 0.001 M HCl solution is …

a)10 b)3 c) 2 d)11

July 2023:- 1) The dissociation constant of NH_4OH is 1.8×10^{-5}. The degree of disso^n in its 0.01M sol^n is ….

a)0.04242 b)0.4242 c)0.004242 d) 4.242

2) Define Buffer soln,write its 4 application.

feb 2023:- 1) The pH of a weak monoacidic base is 11.2, its OH^- ion concentration is ….mol.dm^{-3}

a)1.585×10^{-3} b)3.010×10^{-11}

c) 3.010×10^{-3} d)1.585×10^{-11}

2) Define acidic buffer solution. Write the relation bet^n solubility & solubility product for PbI_2 .

3) A weak monobasic acid is 10% dissociated in 0.05M sol^n. What is the %dissociation in 0.15M sol^n

July-22 :- 1) pH of a sol^n is 3.12, Find its $[H_3O^{\oplus}]$

Feb 2022 :- 1) The value of $[H_3O^+]$ in mol lit^{-1} of 0.001M acetic acid solution is …..(Ka = 1.8×10^{-5})

a)1.34×10^{-1} b)1.34×10^{-2}

c)1.34×10^{-3} d)1.34×10^{-4}

2) Calculate pH of a buffer solution composed of 0.01 M weak base BOH & 0.02 M of its salt BA.

(K_b =1.8×10^{-5} for weak base) ….(3 mark)